Separation of Heavy Water from Water-Isotopes Mixture in Flat-Plate Thermal Diffusion Columns with Transverse Sampling Streams and Optimal Plate Spacing

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Abstract

The effects of plate spacing on the separation of heavy water from water-isotopes mixture in flat-plate thermal diffusion columns with transverse sampling stream, have been investigated. Considerable improvement in performance with fixed operating expense is obtainable if the plate spacing is suitably adjusted, resulting in suppressing the undersirable remixing effect while still preserving the desirable cascading effect.

Key Words: Thermal Diffusion, Heavy Water, Transverse Sampling Stream

1. Introduction

If a temperature gradient is applied to a homogeneous solution, a concentration gradient is usually established, called thermal diffusion effect. The phenomenon of thermal diffusion was first discovered by Enskog [1] from theoretical consideration of the kinetic theory of a mixture of gases and was later demonstrated experimentally by Chapman and Dootson [2]. Thus, a temperature gradient in a mixture of two gases or liquids gives rise to concentration gradients with one component concentrated near the hot wall and the other component concentrated near the cold wall, resulting in separation of mixtures.

In static systems, which were used in the early work of thermal diffusion, the temperature gradient was established in the vertical direction and there was such that the flux due to ordinary diffusion counterbalanced that resulting from thermal diffusion. The steady-state separation obtainable from such a single, static stage was generally so slight that it was of theoretical interest only. It was the great achievement of Clusius and Dickel [3,4] to point out that convective currents could be utilized to produce a cascading effect analogous to the multistage effect of countercurrent extraction and thus obtain a relatively large separation.

In addition to being the resource of fusion energy, deuterium oxide (D_2O) is also the most feasible moderator and coolant for fission reactors. Lewis [5] concentrated a large quantity of water to a small amount of nearly pure heavy water (D_2O) by electrolysis. Between 1940 and 1945, four heavy water production plants were placed in operation by the US Government under the Manhattan Program [6,7]. Thermal diffusion is a well-established method for separating isotopes. It was used to separate uranium isotopes at Oak Ridge Laboratory in World War II. This method is particularly attractive for the separation of hydrogen isotopes because of large ratio in molecular weights.

2. Separation Theory

2.1 Transport Equation

A practical column utilizing thermal diffusion effect consists essentially of two opposing vertical plates separated by a very narrow open space, as shown in Figure 1 for enrichment of heavy water from water-isotopes mixture (H_2O-HDO-D_2O). One plate is heated and the other

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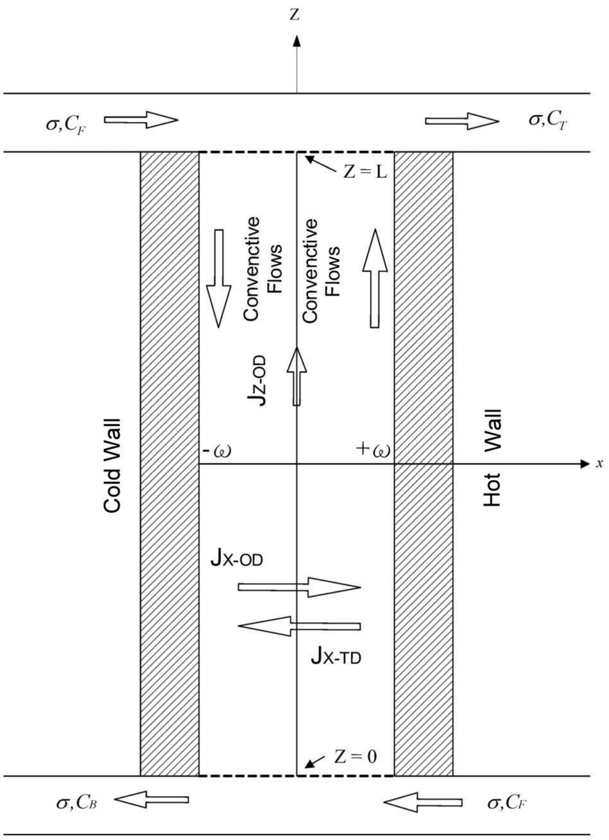

Figure 1. Flows and fluxes in a flat-plate thermal-diffusion column with transverse sampling streams.

cooled, and thermal diffusion effect causes heavy water to diffuse preferentially toward the cold plate with the flux $J_{X\text{-}TD}$. At the same time, the density gradient which arises because of the temperature difference causes smooth laminar convection currents up the hot plate and down the cold plate. Because of the concentration gradient set up by thermal diffusion, the convective currents transport heavy water preferentially toward the bottom and thus create large concentration differences between the bottom and the top of the column. Meanwhile, the concentration gradients in x and z directions produce the fluxes, $J_{X\text{-}OD}$ and $J_{Z\text{-}OD}$, respectively, due to ordinary diffusion, to counterbalance that resulting from thermal diffusion and convection at steady state. Yeh and Yang [8] combined all effects of above flows and fluxes and gave the transport equation for separation of heavy water from water-isotope mixture in a thermal diffusion column as

$$\tau = \mathrm{HA} - \mathrm{K}\frac{dC}{dz} < 0 \text{ (moving toward the bottom of column)} \tag{1}$$

where

$$\mathrm{H} = \frac{\alpha\rho\beta g(2\omega)^3\mathrm{B}(\Delta\mathrm{T})^2}{6!\mu\overline{\mathrm{T}}} < 0 \tag{2}$$

$(\because \alpha < 0 \text{ for } H_2O\text{-}HDO\text{-}D_2O \text{ system})$

$$\mathrm{K} = \frac{\alpha\beta^2 g^2(2\omega)^7\mathrm{B}(\Delta\mathrm{T})^2}{9!D\mu^2} < 0 \tag{3}$$

$$\begin{aligned}\mathrm{A} = C_F[&0.05263 - (0.05263 - 0.0135\mathrm{K}_{eq})C_F \\ &- 0.027\{C_F\mathrm{K}_{eq}(1 - 0.25\mathrm{K}_{eq})C_F\}^{1/2}]\end{aligned} \tag{4}$$

in which K_{eq} is the mass fraction equilibrium constant of the H_2O-HDO-D_2O system.

2.2 Degree of Separation

Making material balance for the top and bottom parts of the column, one obtains, respectively

$$\tau = \sigma(C_T - C_F) \tag{5}$$

$$= \sigma(C_F - C_B) \tag{6}$$

The integration of Eq. (1) coupled with the use of Eqs. (5) and (6) from the top to the bottom of the column, which satisfies the boundary conditions:

$$\mathrm{C} = \mathrm{C_B} \text{ at } z = 0 \tag{7}$$

$$\mathrm{C} = \mathrm{C_T} \text{ at } z = \mathrm{L} \tag{8}$$

are

$$C_T - C_B = \left[A - \frac{\sigma}{\mathrm{H}}(C_T - C_F)\right]\frac{\mathrm{H}L}{\mathrm{K}} \tag{9}$$

$$C_T - C_B = \left[A - \frac{\sigma}{\mathrm{H}}(C_F - C_B)\right]\frac{\mathrm{H}L}{\mathrm{K}} \tag{10}$$

Addition of Eqs. (9) and (10) gives the equation for calculating the degree of separation:

$$\Delta = C_B - C_T \tag{11}$$

$$= \frac{\mathrm{A}(-\mathrm{H}L/\mathrm{K})}{1 + (\sigma L/2\mathrm{K})} \tag{12}$$

3. Optimal Plate Spacing for Best Performance

As mentioned earlier, the plate spacing (2ω) in a thermal diffusion column is generally so small that changing (2ω) will not cause any additional fixed charge. The expenditure of making a separation by thermal diffusion essentially includes two parts: a fixed charge and an operating expense. The fixed charge is roughly proportional to the equipment cost, while the operating expense is chiefly heat. The heat-transfer rate is obtainable from the expression, KBL($\Delta T/2\omega$). Based on these terms, we shall account of the influence of plate-spacing change on the degree of separation, production rate and column length with the consideration of fixed operating expense (i.e. ($\Delta T/2\omega$) is constant). Accordingly, two constants, a and b, are defined from Eqs. (2) and (3) as

$$a = \frac{(-\alpha)\beta g B(\Delta T/2\omega)^2}{6!\mu\overline{T}} = -H/(2\omega)^5 \tag{13}$$

$$b = \frac{\rho\beta^2 g^2 B(\Delta T/2\omega)^2}{9!D\mu^2} = K/(2\omega)^9 \tag{14}$$

and Eq. (12) may be rewritten for Δ, σ and L as

$$\Delta = 2\mathrm{A}a(2\omega)^5/[\{2b(2\omega)^9/L\} + \sigma] \tag{15}$$

$$\sigma = \frac{2\mathrm{A}a(2\omega)^5}{\Delta} - 2b(2\omega)^9/L \tag{16}$$

$$L = \frac{2b(2\omega)^9}{[2\mathrm{A}a(2\omega)^5/\Delta] - \sigma} \tag{17}$$

3.1 Maximum Degree of Separation

The optimal plate-spacing $(2\omega)_\Delta$ for maximum degree of separation Δ_{max} with flow rate σ, column lengthy L and feed concentration $C_{3,F}$ as well as A specified is obtained by partially differentiating Eq. (15) with respect to (2ω) and setting $\partial\Delta/\partial(2\omega) = 0$. After differentiation and simplification, we obtain

$$(2\omega)_\Delta = \left(\frac{\sigma L}{1.6b}\right)^{1/9} \tag{18}$$

If Eq. (18) is substituted into Eq. (15), the maximum degree of separation is given by the following expression:

$$\Delta_{max} = \left(\frac{8\mathrm{A}a}{9\sigma}\right)\left(\frac{\sigma L}{1.6b}\right)^{5/9} = 0.6846\mathrm{A}a(L/b)^{5/9}\sigma^{-4/9} \tag{19}$$

3.2 Maximum Production Rate

The optimal plate-spacing $(2\omega)_\sigma$ for maximum production rate σ_{max} with the degree of separation Δ, column length L and feed concentration $C_{3,F}$ as well as A specified, is obtained by partially differentiating Eq. (16) with respect to (2ω) and setting $\partial\sigma/\partial(2\omega) = 0$. After differentiation and simplification, one has

$$(2\omega)_\sigma = \left(\frac{5AaL}{9b\Delta}\right)^{1/4} \tag{20}$$

If Eq. (20) is substituted into Eq. (16), the maximum production rate is given by the following expression:

$$\sigma_{max} = 0.426\left(\frac{L}{b}\right)^{5/4}\left(\frac{Aa}{\Delta}\right)^{9/4} \tag{21}$$

3.3 Minimum Column Length

To find the minimum column length L_{min} required to accomplish the specified values of Δ, σ and C_F as well as A, we partially differentiate Eq. (17) with respect to (2ω), resulting in

$$(2\omega)_L = \left(\frac{9\sigma\Delta}{8Aa}\right)^{1/5} \tag{22}$$

If Eq. (22) is substituted into Eq. (17), the minimum column length is given by the following expression:

$$L_{min} = 1.978b\left(\frac{\Delta}{Aa}\right)^{9/5}\sigma^{4/5} \tag{23}$$

4. Improvement in Performance

4.1 Numerical Example

The improvement in performance resulting from operating at the optimum plate spacing with fixed operating expense may be illustrated numerically by using the experimental data of previous work [8]. The conditions are: water-isotopes mixture (H_2O-HDO-D_2O system); $\Delta T = 47 - 14 = 33$ °C, $\overline{T} = 30.5$ °C, (2ω) = 0.016 in. =

0.0406 cm, L = 177 cm, B = 10 cm, -H = 1.47 × 10^{-4} g/s = 0.53 g/h, K = 1.549 × 10^{-3} g cm/s = 5.58 g cm/h, K_{eq} = 3.793 at 30.5 °C, a = 4.807 × 10^{6} g/cm^3 h, b = 1.86 × 10^{13} g/cm^8 h, $\Delta T/2\omega$ = 751.23 K/cm.

4.2 Result and Discussion

The improvement in separation by operating at the optimum plate spacing $(2\omega)_\Delta$ is best illustrated by calculating the percentage increase in separation based on the specified column with 2ω = 0.0406 cm, which was employed in previous experimental work [8].

$$I_\Delta = \frac{\Delta_{\max} - \Delta_O}{\Delta_O} \tag{24}$$

Similary, the improvement in output and column length may be defined as

$$I_\sigma = \frac{\sigma_{\max} - \sigma_O}{\sigma_O} \tag{25}$$

$$I_L = \frac{L_O - L_{\min}}{L_0} \tag{26}$$

where Δ_o, σ_o and L_o are the performance obtained in the specified column with 2ω = 0.0406 cm.

From the numerical values and Table 1 given, the optimum plate spacings [$(2\omega)_\Delta$, $(2\omega)_\sigma$, $(2\omega)_L$] and the corresponding performances ($\Delta_{\max}$, $\sigma_{\max}$, $L_{\min}$, I_Δ, I_σ, I_L), as well as the performances obtained in the specified column (2w = 0.0406 cm), are calculated from the appropriate equations. The results are shown in Tables 2–4.

The comparison of recovery, $\Delta_{\max}$ and Δ_o, obtainable at the corresponding optimum plate spacing $(2\omega)_\Delta$ and at (2ω) = 0.0406 cm, respectively, under various flow rates and feed concentrations, is shown in Table 2. It is seen from this table as well as from Eq. (18) that the optimum plate spacing for maximum separation increases with the flow rate. The improvement in separation I_Δ is really obtained, especially for low flow-rate operation.

The comparison of production rates, $\sigma_{\max}$ and σ_o, obtainable at the corresponding optimum plate spacing $(2\omega)_\sigma$ and at (2ω) = 0.0406 cm, respectively, under various feed concentrations and degrees of separation is pre-

Table 1. Some values of A defined in Eq.(4) with K_{eq} = 3.793 at $\bar{T} = 30.5$ °C [8]

$C_{3,F}$	0.1	0.3	0.5	0.7	0.9
A × 10^2	0.359	0.709	0.761	0.591	0.237

Table 2. Comparison of the degree of separation obtained at $(2\omega)_\Delta$ and at (2ω) = 0.0406 cm

C_F	σ (g/h)	Δ_D/A	Δ_o (%)	$(2\omega)_\Delta$ (cm)	$(\Delta T)_\Delta$ (K)	$\Delta_{\max}$ (%)	I_Δ (%)
0.1	0.005	15.598	1.817	0.0314	23.59	3.043	67
0.1	0.01	14.529	1.693	0.0339	25.47	2.236	32
0.1	0.02	12.779	1.489	0.0364	27.34	1.643	10
0.1	0.04	10.297	1.200	0.0396	29.75	1.207	1
0.3	0.005	15.598	2.073	0.0314	23.59	3.471	67
0.3	0.01	14.529	1.931	0.0339	25.47	2.551	32
0.3	0.02	12.779	1.698	0.0364	27.34	1.874	10
0.3	0.04	10.297	1.368	0.0396	29.75	1.377	1
0.5	0.005	15.598	1.725	0.0314	23.59	2.888	67
0.5	0.01	14.529	1.607	0.0339	25.47	2.123	32
0.5	0.02	12.779	1.413	0.0364	27.34	1.560	10
0.5	0.04	10.297	1.139	0.0396	29.75	1.146	1
0.7	0.005	15.598	1.132	0.0314	23.59	1.896	67
0.7	0.01	14.529	1.055	0.0339	25.47	1.393	32
0.7	0.02	12.779	0.928	0.0364	27.34	1.024	10
0.7	0.04	10.297	0.748	0.0396	29.75	0.752	1
0.9	0.005	15.598	0.401	0.0314	23.59	0.671	67
0.9	0.01	14.529	0.373	0.0339	25.47	0.493	32
0.9	0.02	12.779	0.328	0.0364	27.34	0.362	10
0.9	0.04	10.297	0.265	0.0396	29.75	0.266	1

sented in Table 3. It is shown in Table 3 as well as in Eq. (20) that the optimum plate spacing for maximum production rate decreases when the specified degree of separation (Δ/A) increases. The improvement in production rate I_σ is really obtained, especially for higher value of (Δ/A).

Table 4 shows the minimum column length L_{min} and the corresponding optimum plate spacing $(2\omega)_L$ under various flow rates, feed concentrations and specified degrees of separation. It is seen from this table as well as from Eq. (22) that the optimum plate spacing for minimum column length increases as the specified value of ($\sigma\Delta/A$) decreases. The improvement in column length is really obtained, especially for low value of ($\sigma\Delta/A$).

It is shown in Tables 2–4 that the optimum plate spacings [$(2\omega)_\Delta$, $(2\omega)_\sigma$, $(2\omega)_L$] decrease when the improvements in performance (I_Δ, I_σ, I_L) increase. Although the plate spacing in a thermal diffusion column is generally so small that changing (2ω) will not cause any additional or deductible fixed change. However, decreasing (2ω) will also lead to decreasing the suitable temperature differences [$(\Delta T)_\Delta$, $(\Delta T)_\sigma$, $(\Delta T)_L$] between two vertical plates of the column in order to maintain the operating cost ($k\Delta T/2\omega$) constant and, therefore, some operating cost may be deducted to maintain the lower temperature differences. The appropriate temperature differences for maintaining the constant values of ($\Delta T/2\omega$) are also listed in the tables.

Table 3. Comparison of production rates obtained at $(2\omega)_\sigma$ and at (2ω) = 0.0406 cm

Δ/A	σ_o (g/h)	$(2\omega)_\sigma$ (cm)	$(\Delta T)_\sigma$ (K)	σ_{max} (g/h)	I_σ (%)
15.598	0.005	0.0357	19.31	0.016	220
14.529	0.01	0.0367	19.85	0.187	177
12.779	0.02	0.0376	20.33	0.025	25
10.297	0.04	0.0394	21.31	0.041	3

4.3 Sensitivity Analysis of Plate Spacing

Thermal diffusion effect increases with the plate length L and the temperature gradient $\Delta T/2\omega$, especially when the plate spacing (2ω) decreases. Since the separations of isotope mixtures are very difficult and for enhancing the separation, the thermal diffusion column with large column length of 177 cm and small plate spacing of 0.04 cm was employed for separation of water isotope in the previous work [8]. As seen in Eqs. (2) and (3), there are hight powers of (2ω) in the transport coefficients, H and K. Therefore, the plate spacing affects the separation efficiency very sensitively, and the fabrication and assembly of a thermal diffusion column with such small plate spacing should be done very precisely. In the case of encountering the difficulity in fabrication and assembly, one may rather enlarge (2ω) coupled with the increase of ΔT to keep ($\Delta T/2\omega$) unchanged. However, this may lead to the additional cost for maintaining higher temperature on the hot plate, or lower temperature on the cold plate.

5. Conclusion

Nuclear energy has been playing an important role in fulfilling society's energy requirements. It has been realized that heavy water, D_2O, is the most feasible moderator and coolant used in fission reactors to furnish excess neutrons, which may be absorbed by materials other than uranium. Thermal diffusion is an unconventional process for separating liquid or gas mixtures. It is a powerful purification technique used to concentrate desired highly valuable materials, especially for separation of the mixtures of large ratio in molecular weight.

The equations which may be employed to predict the optimum plate spacing for separation of heavy water from water-isotopes mixture in a flat-plate thermal-diffusion column with transverse sampling streams, have been derived in present study. They are Eqs. (18) and (19) for the

Table 4. Comparison of column lengths obtained at $(2\omega)_L$ and at (2ω) = 0.0406 cm

Δ/A	σ (g/h)	L_O (cm)	$(2\omega)_L$ (cm)	$(\Delta T)_L$ (K)	L_{min} (cm)	I_L (%)
15.598	0.005	177	0.0283	21.26	70.00	60
14.529	0.01	177	0.0321	24.11	107.25	39
12.779	0.02	177	0.0359	26.97	148.21	16
10.297	0.04	177	0.0395	29.67	174.94	1

maximum separation, Eqs. (20) and (21) for the maximum production rate, and Eqs. (22) and (23) for minimum column. The improvement in performance was illustrated by employing the experimental data obtained in previous work, and the results are presented in Tables 2–4. It has been shown in these tables that substantial improvement in performances for separation of heavy water from water-isotopes mixture in a flat-plate thermal diffusion column transverse sampling streams can be achieved if the plate spacing is suitably adjusted.

6. List of Symbols

A	pseudo-production form of concentration for D_2O defined in Eq. (4)
a	constant defined by Eq. (13) (g/cm^5s)
B	column width, cm
b	constant defined by Eq. (14) (g/cm^8s)
C	fractional mass concentration of heavy water
C_B, C_T	C in the product streams exiting from bottom end, from top end
C_F	C in feed stream
D	mass diffusivity (cm^2/s)
g	gravitational acceleration (cm/s^2)
H	transport coefficient defined by Eq. (2), g/s
I_Δ, I_σ, I_L	improvement in performances defined by Eqs. (24), (25) and (26), respectively
J_{x-OD}, J_{x-TD}	mass flux in x direction due to ordinary diffusion, thermal diffusion (g/m^2s)
J_{Z-OD}	mass flux in z direction due to ordinary diffusion (g/m^2s)
K	transport coefficient defined by Eq. (3), g cm/s
K_{eq}	mass fractional equilibrium constant of H_2O-HDO-D_2O system
L	column length (cm)
L_{min}	minimum value of L (cm)
L_o	L obtained in a column with 2ω specified (cm)
$\overline{T}$	average absolute temperature of fluid (K)
z	axis parallel to the transport direction (cm)

6.1 Greek Letters

α	reduced thermal diffusion constant, < 0
β	$-(1/\rho)(\partial\rho/\partial T)$ evaluated at $\overline{T}$ (1/K)
Δ	$C_B - C_T$, degree of separation for heavy water
Δ_{max}	maximum value of Δ
Δ_o	Δ obtained in a column with 2ω specified
ΔT	temperature difference between hot and cold surfaces (K)
$(\Delta T)_\Delta$, $(\Delta T)_{2\omega}$, $(\Delta T)_L$	ΔT for the best performances (K)
μ	fluid viscosity (cP)
ρ	fluid density at $\overline{T}$ (g/cm^3)
σ	mass flow rate (g/s)
σ_{max}	maximum value of σ (g/s)
σ_o	σ obtained in a column with 2ω specified (g/s)
2ω	plate spacing of the column (cm)
$(2\omega)_\Delta$, $(2\omega)_\sigma$, $(2\omega)_L$	optimal value of (2ω) for $\Delta_{D,\max}$, for σ_{max}, for L_{min} (cm)

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